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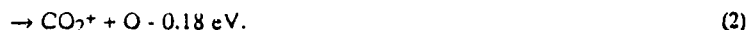
Energy Disposal in the Products of the Reaction $O^+ + CO_2 \rightarrow O_2^+ + CO$

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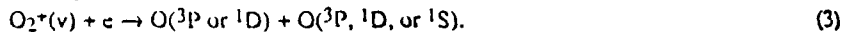
Abstract: The reaction $O^+ + CO_2 \rightarrow O_2^+ + CO$ is exothermic by 1.19 eV. Although spin forbidden for reactants and products in their ground states, the reaction is fast ($k = 9.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) at thermal energies. Ion beam experiments in the energy range from 0.8 to 6.5 eV (lab) show that the translational exothermicity of the reaction (the reaction enthalpy which is converted to translational energy of the products) is negative and equal to the relative energy. The product(s) in these beam experiments must therefore be excited. Experiments in a selected ion flow tube at temperatures of 88 K, 150 K, and 300 K, using the monitor ion technique to determine the vibrational energy distribution in the O_2^+ product, show that the majority of the O_2^+ ions formed in the reaction of O^+ with CO_2 at thermal energies are vibrationally excited. The principal ion product energy level appears to be $O_2^+ (v = 1)$, with a population of about 45% of the total O_2^+ production.

INTRODUCTION

The ion-molecule reaction between O^+ and CO_2 is of interest because of its importance in combustion phenomena, in chemical release experiments in the earth's ionosphere, and in the ionospheres of Mars and Venus. The reaction has long been known to be fast and to proceed through two channels [1], the branching ratio being strongly energy dependent.



The reaction converts an atomic ion, whose recombination with electrons is slow, into a molecular ion, whose recombination is fast. The exothermicity of reaction (1) permits the formation of O_2^+ in vibrational energy levels up to $v = 5$ and of CO up to $v = 4$. Because the electronic states of the products of recombination of O_2^+ (reaction (3)) depend strongly upon the vibrational energy levels of the O_2^+ [2,3,4], it is important to know the vibrational energy content of the products of reaction (1).



The present study summarizes the results of some ion beam experiments, in which the formation of internally excited products at beam energies was established, and of some recent ion flow tube experiments, in which the production of vibrationally excited O_2^+ in reaction (1) was measured.

EXPERIMENTAL

In the ion beam experiment, the translational energies of reactant and product ions were determined using time-of-flight (TOF) techniques. The apparatus and method have been described [5]. In brief, the apparatus consisted of a magnetic mass spectrometer (90 degree sector, 2.54 cm radius) to select the reactant ion species, a decelerating lens, a collision chamber, and a quadrupole mass filter to analyze reactant and product ion species. Single collision conditions obtained. The reactant ion beam was pulsed, and times of flight of reactant and product ions were measured using digital TOF logic. The reactant ion translational energies ranged from 0.8 to 6.5 eV (lab) in the TOF experiments, although reaction cross sections could be measured over the range of reactant ion energies from about 0.2 eV to several tens of eV. At energies below a few eV, the energy spread (FWHM) of the beam was about 0.3 eV.

A variable temperature-selected ion flow tube was used to make the measurements of the rate constants for reaction (1) and of the vibrational energy distribution in the O_2^+ product of this reaction. The apparatus and the method for measuring rate constants have been described [6] and will not be discussed further. In order to determine whether vibrationally excited levels of O_2^+ result from reaction (1), O_2^+ was generated in the flow tube by this reaction. Xe was simultaneously admitted to the flow tube. The charge transfer reaction of $O_2^+(v=0)$ with Xe is slightly endothermic [7] and is therefore slow. The charge transfer reaction(s) of $O_2^+(v \geq 1)$ with Xe are exothermic and fast [8]. The O_2^+ signal level was measured as the flow rate of Xe was varied, producing a decay curve. Three separate portions of the decay curve could be distinguished, suggesting the formation of three (or more) vibrational energy levels in the O_2^+ . (These measurements were subsequently repeated at different CO_2 flow rates to check for systematic differences arising from quenching of $O_2^+(v \geq 1)$ by CO_2).

The three separate portions of the decay curve were identified with particular O_2^+ vibrational energy levels as follows. O_2^+ was produced in the ion source and was injected into the flow tube at different energies in the range from 15 to 100 eV (lab). The distribution of O_2^+ vibrational levels resulting from collisions of the O_2^+ with the helium carrier gas is expected to vary with injection energy and to shift toward higher levels with increasing injection energy. The O_2^+ was titrated with Xe as described above. At the lowest injection energies, over 80% of the O_2^+ reacted only very slowly with Xe and is therefore believed to be in the lowest vibrational level. The remaining O_2^+ was presumed to be in the first excited vibrational level.

The injection energy was then increased, and the experiment was repeated for several injection energies. As discussed below, decay curves were obtained similar to those obtained when the O_2^+ was generated from reaction (1) in the flow tube. In order to determine the population of vibrational levels of the O_2^+ , the gases SO_2 and H_2O were used as monitors. The ionization potential (IP) of SO_2 , which is 12.34 eV, compares with the recombination energy (RE) of $O_2^+(v = 2)$, which is 12.49 eV. (The RE is the energy available in the process in which a positive ion, AB^+ , and a free electron combine to produce AB in its lowest energy state). The IP of H_2O is 12.62 eV, and the RE of $O_2^+(v = 3)$ is 12.71 eV. Charge transfer between SO_2 and $O_2^+(v \geq 2)$ is thus exothermic, as is that between H_2O and $O_2^+(v \geq 3)$. In the experiments at 300K, SO_2 and H_2O were admitted to the flow tube, and the resulting decay of the O_2^+ signal level was taken as a measure of the populations of $O_2^+(v \geq 2)$ and of $O_2^+(v \geq 3)$, respectively. The fractional populations of the individual levels $v=0,1,2$, and of the combined levels $v \geq 3$ were then obtained by difference. In the experiments at 150K, SO_2 and H_2O could not be used as monitor gases because of their low vapor pressures at that temperature, and CH_4 (IP = 12.55 eV) was used instead. Because of space limitations, details of the chemistry resulting from the use of SO_2 , H_2O , and CH_4 as monitor gases must be omitted here.

RESULTS AND DISCUSSION

For any reaction (written here as an ion-molecule reaction)



the difference between the translational energies of the products and the translational energies of the reactants is the translational exothermicity, Q , and is the energy converted in the reaction from internal energy to translational energy. Q is thus defined by eq. (5)

$$Q = E_3 + E_4 - E_1 - E_2 \quad (5)$$

Experimentally, Q can be obtained from eq. (6):

$$Q = \left\{ \left(\frac{m_2}{m_4} - 1 \right) \langle E_2 \rangle + \left(\frac{m_1}{m_4} - 1 \right) E_1 + \left(\frac{m_3}{m_4} + 1 \right) E_3 - \right. \\ \left. (2/m_4) (m_1 m_3 E_1 E_3)^{1/2} \cos \theta \right\} \quad (6)$$

In eq. (6) the subscripts $i = 1,2,3,4$ refer to species A^+ , B , C^+ , and D , respectively, of mass m_i and laboratory kinetic energy E_i , and $\langle E_2 \rangle$ means average kinetic energy of the reactant neutral gas, i.e., $3/2kT$. The angle θ is the scattering angle for species C^+ relative to the direction of the incident ion beam and is taken as zero here for the longitudinal double mass spectrometer system. Eq. (6) can be derived from conservation of energy and linear momentum [9,10].

Table 1 summarizes the results of the TOF experiments for both reactions (1) and (2). At all energies in the range studied, Q is negative, i. e., translational energy of the reactants has been converted into internal energy of the products. In each case, Q is very nearly equal to the barycentric energy available, indicating that all of the available translational energy in the

reactants is converted to internal energy of the products (or in reaction (2) is partially used in overcoming the small reaction endothermicity) and that the reaction exothermicity, in the case of reaction (1) as written for ground states, is retained as internal energy of the products. Under the conditions of these beam experiments, then, the product(s) of the reaction of O^+ with CO_2 must be internally excited. The flow tube experiments were then undertaken in order to determine whether the products of the reaction at thermal energies are excited and how that excitation is distributed.

A typical set of the raw data used to determine the distribution of vibrational energy in the O_2^+ product of reaction (1) is shown in Fig. 1. Here the O_2^+ is generated in the flow tube by reaction (1). Decay of the O_2^+ signal level is measured as a function of Xe flow rate. As noted above, charge transfer between O_2^+ ($v = 0$) and Xe is slightly endothermic and slow, while that between O_2^+ ($v \geq 1$) is exothermic and fast. If a single vibrational level were present in the O_2^+ or, improbably, if all levels present reacted with similar rate constants, then the decay curve would be linear over at least a few decades. The observed curvature suggests that more than one vibrational energy level is present. At Xe flow rates above about 25 scm ($1 \text{ scm} = 1 \text{ atm cm}^3 \text{ min}^{-1}$ at 298 K), the decay does become linear, indicating that all of the faster reacting O_2^+ ($v \geq 1$) has reacted and that only O_2^+ ($v = 0$) remains. The decay rate in this part of the curve is close to that observed when O_2^+ is injected into the flow tube at low energies such that O_2^+ ($v = 0$) is the predominant species present. The agreement is not exact because the source of the O_2^+ , when it is generated in the flow tube by reaction (1), is distributed along the entire reaction region, rather than arising as a point source, as it is when injected directly. A least squares line can be drawn through the linear part of the decay curve and extrapolated to zero flow rate of Xe. The intercept is then proportional to the amount of O_2^+ ($v = 0$) produced in reaction (1). This line can be subtracted point by point from the original decay curve to yield the signal level corresponding to the vibrationally excited O_2^+ . The resulting line also exhibits curvature, suggesting that at least two vibrationally excited levels of O_2^+ are produced in reaction (1). Again a least squares line can be drawn through the points at high Xe flow rates, extrapolated to zero flow rate, and subtracted. The result is a set of points linear to within experimental error. The fractional populations of the various vibrational levels can then be obtained by comparison with the total O_2^+ signal level. We shall refer to the three separate components of the decay curve as the slow, medium, and fast reacting constituents, respectively.

While it is clear that the slow reacting constituent of the O_2^+ decay curve corresponds to O_2^+ ($v = 0$), it is not obvious which vibrational levels are responsible for the medium and fast reacting constituents. Information on this problem was obtained from the experiments in which O_2^+ was injected into the flow tube at varying injection energy. Table 2 summarizes these

experiments at 150 K. The relative abundances given in this Table were obtained by extrapolating the linear components of the decay curve to zero flow rate of Xe and comparing the values at the intercept to the total signal level of O_2^+ . When a high injection energy, e. g., 60 eV, was used, the decay curve resulting from attenuation by Xe could be resolved into three linear components. The ratio of the slopes of these three components is the same as that found when the O_2^+ is generated by reaction (1) in the flow tube. At low injection energies, the decay curve could be resolved into only two components, and these corresponded to the slow reacting constituent and the fast reacting constituent; the medium reacting constituent was absent. In addition, when only these two constituents were present and when SO_2 and H_2O were used as the monitor gases at 300 K, or CH_4 at 150 K, the ionic products that monitor the higher vibrational levels of O_2^+ , $v \geq 2$, were either absent or were present in only low abundance. We suggest, then, that the slow reacting constituent is O_2^+ ($v = 0$), the fast reacting constituent is O_2^+ ($v = 1$), and the medium reacting constituent is O_2^+ ($v \geq 2$).

In order to estimate the fractional populations of the O_2^+ vibrational levels resulting from reaction (1), several runs were made using different flow rates of CO_2 at each temperature. No systematic difference was found in the percentage of each vibrational level as a function of CO_2 flow rate, indicating that no significant quenching of O_2^+ ($v \geq 1$) by CO_2 was occurring. The rate constant for the charge transfer reaction of Xe with O_2^+ ($v = 1$) was measured in the present work as $7.5 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ at 150 K and 9.5×10^{-10} at 300 K (Table 3). Because these rate constants are close to the collision limited values, it is unlikely that Xe also quenches O_2^+ ($v = 1$) at a significant rate. Charge transfer of O_2^+ ($v \geq 2$) with Xe is slower (Table 3), i. e., $k = 6.6 \times 10^{-11}$ at 150 K and 2.1×10^{-10} at 300 K, and quenching of O_2^+ ($v \geq 2$) might compete with charge transfer. The rate constant for quenching of O_2^+ ($v \geq 2$) is not known.

Neglecting the possible complications arising from quenching of O_2^+ ($v \geq 2$) by the monitor gas, the fractional populations of O_2^+ (v) produced in reaction (1) can be estimated as described and are shown in Figure 2. It is evident that most of the O_2^+ is vibrationally excited and that O_2^+ ($v = 1$) is the predominant species at all temperatures studied. At the lower temperatures, more O_2^+ ($v = 0$) and less O_2^+ ($v \geq 2$) are found. If quenching is indeed occurring, then even more of the O_2^+ is produced vibrationally excited than is shown in Figure 2. Assuming that the higher levels correspond only to O_2^+ ($v = 2$), the average vibrational energy content of the products of reaction (1) measured here represents only about 20% of the exothermicity of the reaction. The remaining energy can in principle be divided among vibrational excitation in the CO product, rotational excitation in either or both products, and translational energy. The results of the ion beam experiments show that all of the reaction exothermicity remains as internal energy of the products and thus suggest that the CO may be vibrationally excited as well.

Table 1. Translational exothermicities, Q_1 and Q_2 , for reactions (1) and (2), respectively, as a function of laboratory kinetic energy (KE) of the O^+ reactant ion. Also tabulated are the barycentric energies (E_{cm}) at each lab energy. Energies in eV. Note that the values for Q_1 and Q_2 are negative.

KE	0.79	0.91	0.92	1.7	2.2	2.5	2.9	3.0	5.9	6.5
$-Q_1$	0.58	0.67	0.63	1.2	1.6	1.7	1.9	2.0	4.3	4.7
$-Q_2$	0.58	0.66	0.62	1.2	1.6	1.8	2.1	2.0	4.3	4.7
E_{cm}	0.58	0.67	0.67	1.2	1.6	1.8	2.1	2.2	4.3	4.8

Table 2. Summary of results for O_2^+ injection (150 K). Relative abundances of the $O_2^+(v)$ states which react with Xe at different rates as a function of injection energy.

Injection energy (eV)	$O_2^+(v)$ States		
	Slow	Medium	Fast
15	81%	----	19%
20	76%	----	24%
30	71%	----	29%
45	57%	3-8%	29-34%
60	39%	6%	55%
80	30%	6%	64%
100	25%	7-10%	62-66%

Table 3. Rate constants for various reactions investigated in this study.

Reaction	Rate Constant ($cm^3 s^{-1}$)	
	150 K	300 K
$O^+ + CO_2 \rightarrow O_2^+ + CO$	$9.6 \times 10^{-10} (\pm 25\%)$	$9.6 \times 10^{-10} (\pm 25\%)$
$O_2^+(v=0) + Xe \rightarrow Xe^+ + O_2$	$1.1 \times 10^{-11} (\pm 25\%)$	$5.74 \times 10^{-11} (\pm 25\%)$
$O_2^+(v \geq 2)(a) + Xe \rightarrow Xe^+ + O_2$	$6.6 \times 10^{-11} (+50, -35\%)$	$2.1 \times 10^{-10} (+50, -35\%)$
$O_2^+(v \geq 1) + CO_2 \rightarrow O_2^+(v=0) + CO_2$	$1.9 \times 10^{-10} (+50, -35\%)$	$1 \times 10^{-10} (b)$

(a) The identification of the excited vibrational levels to which the rate constants refer is tentative. Refer to the text for a complete discussion.

(b) This quenching rate constant has not been measured in this study. The value given is due to Böhringer et al.[8] and is included to show the temperature dependence.

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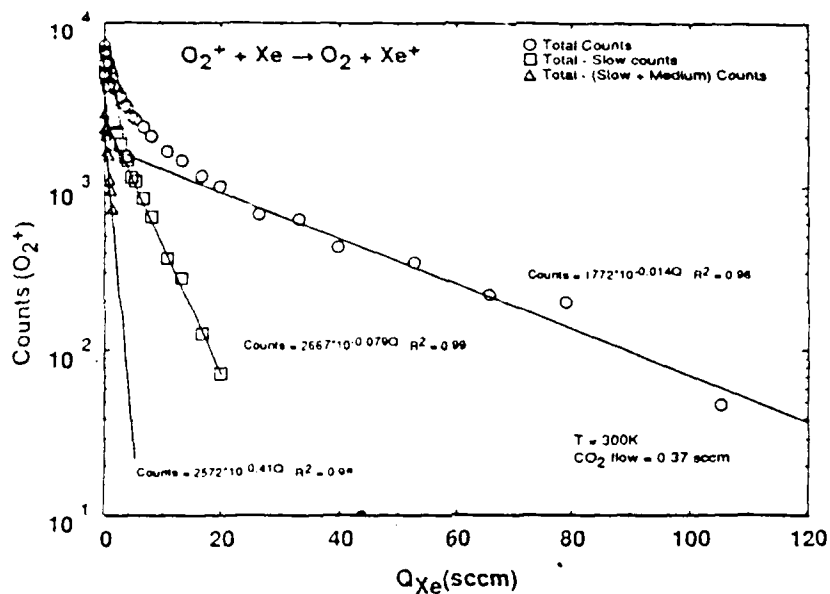


Figure 1. Decay of O_2^+ produced in the reaction of O^+ with CO_2 as function of Xe flow. The data were taken at a temperature of 300 K and a CO_2 flow of 0.37 sccm. Circles refer to the raw data. Squares refer to the total signal minus the least squares line through the linear portion of the curve at high Xe flow. Triangles refer to subtraction of the intermediate least squares line from the square symbols.

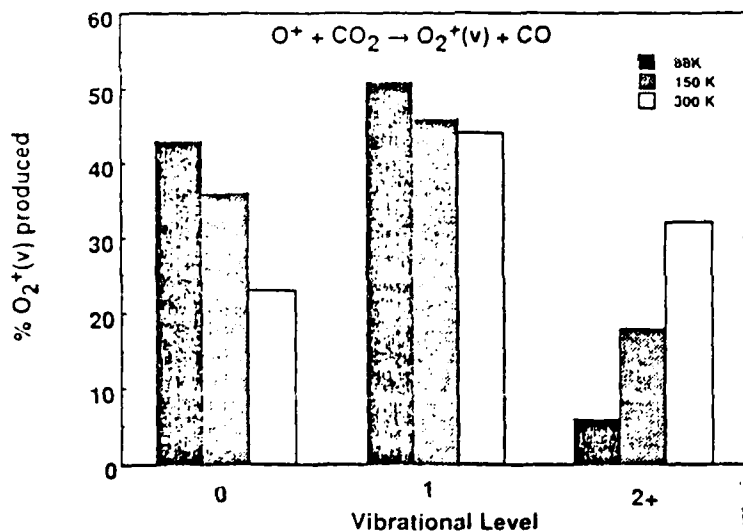


Figure 2. Percent $O_2^+(v)$ produced in the reaction of O^+ with CO_2 as a function of vibrational level. Solid, shaded and clear bars refer to the experimental temperatures 88 K, 150 K and 300 K, respectively.